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(54) Title: NON–SYMMETRICAL FREE RADICAL INITIATORS AND PROCESS FOR USE THEREWITH

(57) Abstract

The present invention relates to non–symmetrical free radical polymerization initiators and for processes which initiate polymerization, and polymerization reactions which are conducted in the presence of said unsymmetrical free radical initiators. The present invention processes allow the formulator to control the type and degree of polymerization due to the initiators of the present invention. The process for initiating polymerization comprises the steps of: (a) reacting a non–symmetrical initiator having the formula: R–N=N–L–A, wherein R is a unit which forms a free radical which does not initiate polymerization; A is a unit which is capable of reacting with a polymer core functional group thereby providing a means for attaching said non–symmetrical initiator to a polymer core; L is a unit capable of forming a free radical moiety having the formula: .L–, said L unit is a substituted or unsubstituted; C_1–C_{10} linear or branched alkylene, C_3–C_{20} arylene, C_4–C_{20} alkyl substituted arylene, C_4–C_{20} alkylarylene, and mixtures thereof; with a polymer core having *n* functional groups capable of reacting with said non–symmetrical initiator to form a conjugate having the formula: $[R–N=N–L–A']_n$–[Core], wherein A' is a linking unit to said polymer core; (b) adding to said conjugate at least one monomer capable of forming a polymer to form a reaction mixture; and (c) initiating polymerization by heating said reaction mixture to a temperature sufficient to form a free radical conjugate having the formula: $[.L–A']_n$–[Core], said temperature from about 0 °C to about 160 °C.

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NON-SYMMETRICAL FREE RADICAL INITIATORS AND PROCESS FOR USE THEREWITH

FIELD OF THE INVENTION

The present invention relates to non-symmetrical free radical polymerization initiators and for processes which initiate polymerization, and polymerization reactions which are conducted in the presence of said unsymmetrical free radical initiators. The present invention processes allow the formulator to control the type and degree of polymerization due to the initiators of the present invention.

BACKGROUND OF THE INVENTION

Polymers are ubiquitous, occuring both in nature and as a result of human endeavor. As polymerization has been utilized to construct new materials which serve to replace or improve naturally occuring materials, methods have been developed to control the parameters of the chemical processes which form the actual polymeric material. Control of these processes has allowed the artisan to tailor polymers to meet specific technical requirements. Polymerization thermodynamics and kinetics are well understood and the application of this knowledge has provided the formulator with a wide array of options for conducting polymerization reactions, *inter alia*, free radical polymerization reactions.

One type of polymerization and category of polymer known as "star" polymers. These types of polymers, unlike linearly propagating or randomly branching polymers, have a requirement that from a basic "core backbone" branches are deliberately built up in a manner wherein each branch has the same relative degree of polymerization and/or branching. However, free radical polymerization reactions which employ conventional initiators may lead to side reactions wherein monomers are added to a propagating chain which is not a branch or otherwise affixed to the polymer core. These impurities are not only wastefully of starting monomer, but change the bulk properties of the resultant polymer, for example, the formulator is left with an admixture of desired star polymer and unwanted linear impurity.

There is therefore, a long felt need in the art for a free radical polymerization initiator which provides a controllable polymerization, especially controllable polymerization of star polymers or other dendrimeric polymers. There is also a long felt need in the art for both processes which suitably initiate said controllable polymerization reactions as well as polymerization reactions which utilize controllable polymerization conditions.

SUMMARY OF THE INVENTION

The present invention meets the aforementioned needs in that it has been surprisingly discovered that certain non-symmetrical free radical polymerization initiators are capable of instigating controllable reactions which allow the formulator to control the relative degree and rate by which concurrently forming polymer chains are formed. The initiators and processes of the present invention are especially adaptable to the art of dendrimeric or "star" polymers.

The first aspect of the present invention relates to a process for initiating polymerization, said process comprising the steps of:

a) reacting a non-symmetrical initiator having the formula:

$$R—N=N—L—A$$

wherein R is a unit which forms a free radical which does not initiate polymerization; A is a unit which is capable of reacting with a polymer core functional group thereby providing a means for attaching said non-symmetrical initiator to a polymer core; L is a unit capable of forming a free radical moiety having the formula:

$$\cdot L—$$

said L unit is a substituted or unsubstituted: C_1-C_{10} linear or branched alkylene, C_3-C_{20} arylene, C_4-C_{20} alkyl substituted arylene, C_4-C_{20} alkylarylene, and mixtures thereof; with a polymer core having *n* functional groups capable of reacting with said non-symmetrical initiator to form a conjugate having the formula:

$$[R—N=N—L—A']_n—[Core]$$

wherein A' is a linking unit to said polymer core;

b) adding to said conjugate a least one monomer capable of forming a polymer to form a reaction mixture; and

c) initiating polymerization by heating said reaction mixture to a temperature sufficient to form a free radical conjugate having the formula:

$$[\cdot L—A']_n—[Core]$$

said temperature from about 0 °C to about 160 °C.

Another aspect of the present invention relates to polymerization processes which utilize the non-symmetrical free radical initiators described herein.

The present invention is yet further directed to non-symmetrical free radical polymerization initiators, preferably triphenylmethylazo compounds which release upon activation at least one active free radical initiator and the balance triphenylmethyl radicals.

These and other objects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims. All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (^{o} C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The preset invention relates to non-symmetrical free radical initiators and to processes for initiating polymerization and processes for conducting polymerization in the presence thereof. The initiators of the present invention are azo initiators which break down to release nitrogen gas and two free radical fragments, said initiators have the general formula:

$$R{-}N{=}N{-}L{-}A$$

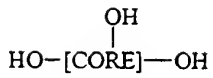
wherein R is a unit which forms a free radical, but said free radical does not initiate or propagate polymerization. The unit -LA serves two purposes. The first is to link the free radical initiator to a core fragment via a linking unit A the second purpose is to form a free radical capable of initiating polymerization. For the purposes of the present invention once the A unit is linked to a core unit or fragment, said A unit is identified by the term A'. As described hereinabove, the L unit serves to form a free radical having the formula:

$$\cdot L{-}{-}$$

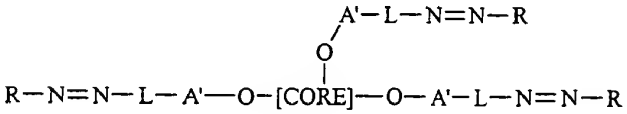
said free radical capable of initiating polymerization in the presence of one or more monomers. In a preferred embodiment, the structure of L will support formation of an active free radical and will be substituted by one or more units which activate said free radical. Preferably the structure of L mimics in part the bulk structure of the monomers which will be propagated by the use of the free radical initiators of the present invention.

Setting forth one problem solved by the non-symmetrical initiators and the process for initiating a polymerization reaction therewith relates to star polymers.

A non-limiting example of the controllable use of the non-symmetrical free radical initiators involves the controlled extension of the three polymer chains which can propagate from the core unit depicted herein. A core having the formula:

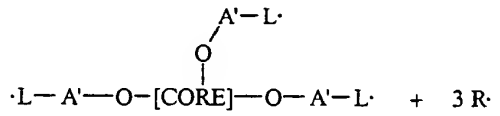


is first reacted with a non-symmetrical initiator to form a conjugate having the formula:



wherein the non-symmetrical initiator has been attached to a moiety of the core unit which is capable of reacting with said initiator. However, by adjusting the stoichiometry of the reactants, the formulator may chose to form a conjugate wherein any number of functional core units remain unreacted with initiators.

The conjugate is then heated to a temperature which forms free radicals having the formula:

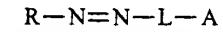


in addition to 3 equivalents of nitrogen gas. The R radicals are radicals which do not initiate polymerization as described herein below. Polymerization can now be controllably conducted at each L sight using one or more monomers which can be added via free radical polymerization.

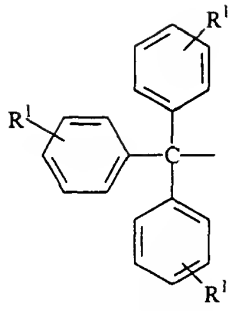
The following is a detailed description of the elements which comprise the present invention.

Non-symmetrical Free Radical Initiators

The non-symmetrical free radical initiators of the present invention have the formula:



wherein R moiety which is capable of forming a stable free radical which does not promote free radical polymerization under the conditions of the processes described herein below. R does not initiate polymerization under the conditions of the present invention processes. Preferably R units are substituted or unsubstituted triphenylmethyl units having the formula:



wherein each R^1 is independently selected from the group consisting of:

a) hydrogen;

b) C_1-C_{12} alkyl;

c) C_3-C_{12} cycloalkyl;

d) C_3-C_{15} substituted or unsubstituted aryl;

e) C_4-C_{15} substituted or unsubstituted alkylenearyl;

f) $-N(R^2)_2$;

g) $-OR^2$;

h) $-SR^2$;

i) and mixtures thereof;

wherein each R^2 is independently selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, C_3-C_{15} substituted or unsubstituted aryl, C_4-C_{15} substituted or unsubstituted alkylenearyl, and mixtures thereof.

R^1 units are preferably any unit which serves to stabilize the free radical R towards non-reactivity and may include one or more substitutions per aryl unit. For example, *para*-methoxy units, *meta*-chloro units and *meta*-alkylamino units are all suitable R^1 units which serve to stabilize the R unit free radical once formed. Preferred R^1 units are hydrogen, methoxy, and mixtures thereof.

Preferred R^2 units are hydrogen, C_1-C_4 alkyl, and mixtures thereof; more preferably hydrogen or methyl.

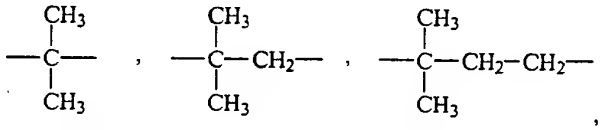
L units are any unit which is capable of forming a free radical moiety having the formula:

·L—

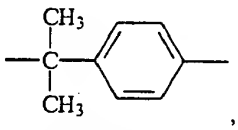
said L unit is an unsubstituted C_1-C_{10} linear or branched alkylene, substituted C_1-C_{10} linear or branched alkylene, unsubstituted C_3-C_{20} arylene, substituted C_3-C_{20} arylene C_4-C_{20} alkyl substituted arylene, unsubstituted C_4-C_{20} alkylarylene, substituted C_4-C_{20} alkylarylene, and mixtures thereof. The preferred L unit is one which promotes the initiation of polymerization. The L units of the present invention may be substituted by moieties which promote the

stabilization or enhance the reactivity of the resulting free radical moiety. A preferred substituted unit is a nitrile substituted alkylene unit. Other preferred L units include arylene units. Preferred L units have a tertiary carbon atom which is adjacent to the azo unit thereby resulting in a tertiary free radical species once the process begins.

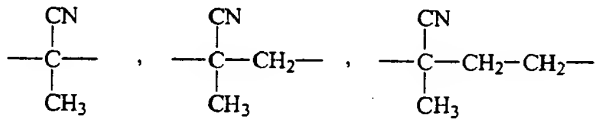
Non-limiting examples of L units include 2,2'-isopropylidene; 1,2-isobutylene; 1,3-isopentylene; having the formulae:



respectively; (4-isopropylidene)-1,4-phenylene having the formula:



1-cyano-1-methylmethylene; 2-cyano-1,2-propylene, and 3-cyano-1,3-butylene having the formulae:

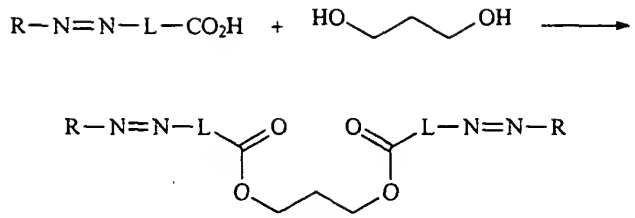


respectively.

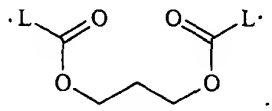
A units serve to attach the free radical initiators of the present invention to a core unit or to an initiator unit. The A units of the present invention once reacted with the core unit or initiator unit are identified herein as A' units. Non-limiting examples of A units include units selected from the group consisting of $-CO_2H$, -COOR', $-NH_2$, -OH, halogen, and mixtures thereof, wherein -OR' is any labile alcohol moiety. Halogen includes fluorine, chlorine, bromine, and iodine.

Non-limiting examples of -LA units include *para*-carboxyphenyl, 2-cyano-4-carboxybut-2-yl; 2-cyano-5-carboxypent-2-yl; 6-carboxy-2-naphthyl; 1-cyano-1-(4-carboxyphenyl)ethyl; and mixtures thereof

An example of attachment of a non-symmetrical initiator to a core includes reaction of two equivalents of the unit $RNNL-CO_2H$ with 1,3-propylene glycol to form a conjugate as depicted in the following scheme:



wherein activation of said conjugate forms a free radical species capable of initiating polymerization, said free radical species having the formula:



For the purposes of the present invention the terms "aryl" and "arylene" relate to aromatic ring systems which comprise only carbon atoms, *inter alia*, phenyl or phenylene, and to ring systems which also comprise heteroatoms, *inter alia*, furyl or furylene. Non-limiting examples of ring systems which are suitable for use in the free radical initiators of the present invention include phenyl, tolyl, xylyl, cumenyl, napthyl, biphenyl, thienyl, furyl, pyrrolyl, pyridinyl, pyrazinyl, thiazolyl, pyrimidinyl, quinolinyl, triazolyl, tetrazolyl, benzothiazolyl, benzofuryl, indolyl, indenyl, azulenyl, fluorenyl, anthracenyl, oxazolyl, isoxazolyl, isotriazolyl, imidazolyl, pyraxolyl, oxadiazolyl, indolizinyl, indolyl, isoindolyl, purinyl, quinolizinyl, quinolinyl, isoquinolinyl, cinnolinyl, and mixtures. The aryl and arylene units described herein can be attached at any suitable point, for example, 1,4-phenylene as well as 1,2-phenylene.

The following are non-limiting examples of non-symmetrical free radical initiators according to the present invention:

2-[(triphenylmethyl)azo]-2-methylpropionic acid;
2-[(4-methoxyphenyldiphenylmethyl)azo]-2-methylpropionic acid;
2-[(triphenylmethyl)azo]-2-cyanopropionic acid;
3-[(triphenylmethyl)azo]-3-methylbutyric acid;
3-[(4-methoxyphenyldiphenylmethyl)azo]-3-methylbutyric acid;
3-[(triphenylmethyl)azo]-3-cyanobutyric acid;
4-[(triphenylmethyl)azo]-4-methylpentanoic acid;
4-[(4-methoxyphenyldiphenylmethyl)azo]-4-methylpentanoic acid;
4-[(triphenylmethyl)azo]-4-cyanopentanoic acid;
4-[1-(triphenylmethylazo)-1-methylethyl]benzoic acid;
4-[1-(triphenylmethylazo)-1-cyanoethyl]benzoic acid;
4-{1-[(4-methoxyphenyldiphenylmethyl)azo]-1-methylethyl}benzoic acid;
6-[1-(triphenylmethylazo)-1-methylethyl]-1-naphthenecarboxylic acid;

6-[1-(triphenylmethylazo)-1-methylethyl]-2-naphthalenecarboxylic acid;

6-{1-[(4-methoxyphenyldiphenylmethyl)azo]-1-methylethyl}-1-naphthenecarboxylic acid;

6-{1-[(4-methoxyphenyldiphenylmethyl)azo]-1-cyanoethyl}-1-naphthenecarboxylic acid;

6-{1-[(4-methoxyphenyldiphenylmethyl)azo]-1-methylethyl}-2-naphthalenecarboxylic acid;

6-{1-[(4-methoxyphenyldiphenylmethyl)azo]-1-cyanoethyl}-2-naphthalenecarboxylic acid;

4-(triphenylmethyl)azobenzoic acid;

4-[(4-methoxyphenyldiphenylmethyl)azo]benzoic acid;

4-{[tri-(3,5-dimethylphenyl)methyl]azo}benzoic acid;

4-{[(3,5-dimethyl-4-methoxyphenyl)-di-(3,5-dimethylphenyl)methyl]azo}benzoic acid.

The following is a non-limiting example of the preparation of a non-symmetrical free radical initiator according to the present invention. The procedure herein below may be modified or adjusted by the artisan according to the conditions required by the particular desired non-symmetrical free radical inhibitor.

EXAMPLE 1

Formation of 4-[(triphenylmethyl)azo]benzoic acid

To a solution of 4-hydrazinobenzoic acid (4 g, 26.3 mmol) in N,N-dimethylformamide (50 mL) is added diisopropylethylamine (9.16 mL, 52.6 mmol), followed by triphenylmethyl chloride (7.7 g, 27.6 mmol). With a drying tube attached, the reaction is allowed to stir at room temperature for 18 hours. The reaction solution is dissolved in 1:1 ethyl acetate / ether (300 mL) washed with dilute HCl and water, dried, and concentrated in vacuo to afford 4-(N'-triphenylmethylhydrazino)benzoic acid.

A 250 mL flask is charged with 4-(N'-triphenylmethylhydrazino)benzoic acid (2 g) and glacial acetic acid (130 mL), and a drying tube is attached. The mixture is stirred for 16 hours, with occasional gentle warming to dissolve the hydrazine. To this solution is added a mixture of ethylenediaminetetraacetic acid (EDTA) (45 mg) and sodium tungstate (12 mg) in water (1 mL), followed by 30% hydrogen peroxide (563 μL). After stirring for 2 hours, the solution is concentrated under reduced pressure and crystallized from hexane to afford 4-[(triphenylmethyl)azo]benzoic acid.

Polymerization Cores

The core to which the non-symmetrical initiator is bonded via the A units can be any compound which is useful for preparing a polymer, *i.e.*, a compound from which one or more polymer chains may propagate. The core can be any which is known in the art, *inter alia*, poly-

functional units which are used to form the core of "star polymers". Each moiety of the core which reacts with the non-symmetrical free radical initiator serves as an arm from which linear polymerization is propagated.

Preferably, the core is a single molecule or linear oligomer having between one and about 100 functional moieties capable of forming a stable covalent bond with the A unit of an unsymmetrical free radical inhibitor of the present invention. Functional moieties capable of forming a stable covalent bond with A include, but are not limited to, carboxylic acids, amines, alcohols, halides, and isocyanates.

Non-limiting examples of suitable cores include discrete molecules such as functionalized aromatics (*e.g.*, functionalized benzene), sugars (*e.g.*, cyclodextrins), functionalized calixaranes, functionalized dendrimers, amines such as ethylenediamine and ammonia, and pentaerythritol. Other examples of suitable cores also include oligomers. Such oligomers can be derived, for example, from functionalized polymerized divinylbenzene; hydroxyethyl methacrylate and methyl methacrylate; acrylic acid and methyl acrylate; and functional siloxanes.

One preferred embodiment of the present invention relates to dendrimeric polymers. Examples of suitable dendrimeric cores are disclosed in "Starburst®/Cascade Dendrimers: Fundamental Building Blocks for a New Nanoscopic Chemistry Set", Tomalia, *Aldrichimica Acta*, Vol. 26, No. 4, pp. 91 - 101 (1993), Tomalia et al., "Starburst Dendrimers: Molecular-Level Control of Size, Shape, Surface Chemistry, Topology, and Flexibility from Atoms to Macroscopic Matter", *Angew. Chem. Int. Ed. Engl.*, Vol. 29, pp. 138 - 175 (1990), and Kazmaier et al., EP 0,735,064, assigned to Xerox Corp., published October 2, 1996.

Non-limiting examples of cores are of the STARBURST® topology, many of which are commercially available from sources such as Aldrich Chemical Co., Milwaukee, WI. For example, Starburst® (PAMAM) Dendrimer, Generation 1, Starburst® (PAMAM) Dendrimer, Generation 2, Starburst® (PAMAM) Dendrimer, Generation 3, and Starburst® (PAMAM) Dendrimer, Generation 4, each available from Aldrich Chemical Co., offer 8, 16, 32, and 64 surface primary amino groups, respectively. Other suitable cores include those sold under the Astramol® name, such as Polypropylenimine Tetraamine Dendrimer, Generation 1.0 (DAB-Am-4) having 4 surface primary amino groups, from Aldrich Chemical Co., Milwaukee, WI. As a further example, Starburst® (PAMAM) Dendrimer, Generation 0.5, Starburst® (PAMAM) Dendrimer, Generation 1.5, Starburst® (PAMAM) Dendrimer, Generation 2.5, and Starburst® (PAMAM) Dendrimer, Generation 3.5, each available from Aldrich Chemical Co., offer 8, 16, 32, and 64 surface primary carboxylate groups, respectively.

The core will have at least one moiety which is capable of reacting with the A unit of the non-symmetrical free radical initiators of the present invention. For example, wherein the core has at least one amine ($-NH_2$) functionality, the core may be coupled with an initiator wherein A

is -CO_2H. Similarly, a core comprising one or more hydroxyl units may be functionalized with the same A unit.

PROCESS OF THE PRESENT INVENTION

The present invention relates to a process for initiating a free radical polymerization reaction. The present invention also relates to a free radical polymerization process utilizing the non-symmetrical free radical initiators of the present invention.

Initiation Process and Polymerization Process

The present invention relates to a process for initiating polymerization comprising the steps of:

a) reacting a non-symmetrical initiator having the formula:

$$R—N=N—L—A$$

wherein R is a unit which is capable of forming a stable free radical and not initiating a free radical polymerization reaction, preferably R is a substituted or unsubstituted triphenylmethyl unit; A is a unit which is capable of reacting with a polymer core functional group thereby providing a means for attaching said non-symmetrical initiator to a polymer core; L is a unit capable of forming a free radical moiety having the formula:

$$\cdot L—$$

said L unit is a substituted or unsubstituted: C_1-C_{10} linear or branched alkylene, C_3-C_{20} arylene, C_4-C_{20} alkyl substituted arylene, C_4-C_{20} alkylarylene, and mixtures thereof; with a polymer core having *n* functional groups capable of reacting with said non-symmetrical initiator to form a conjugate having the formula:

$$[R—N=N—L—A']_n—[Core]$$

wherein A' is a linking unit to said polymer core;

b) adding to said conjugate a least one monomer capable of forming a polymer to form a reaction mixture; and

c) initiating polymerization by heating said reaction mixture to a temperature sufficient to form a free radical conjugate having the formula:

$$[\cdot L—A']_n—[Core]$$

said temperature from about 0 °C to about 160 °C.

The present invention also relates to a polymerization process which utilizes the initiators of the present invention, said process comprising the steps of:

A) initiating polymerization with a non-symmetrical initiator comprising the steps of:

a) reacting a non-symmetrical initiator having the formula:

$$R—N=N—L—A$$

wherein R is a unit which is capable of forming a stable free radical and not initiating a free radical polymerization reaction, preferably R is a substituted or unsubstituted triphenylmethyl unit; A is a unit which is capable of reacting with a polymer core functional group thereby providing a means for attaching said non-symmetrical initiator to a polymer core; L is a unit capable of forming a free radical moiety having the formula:

$$\cdot L—$$

said L unit is a substituted or unsubstituted: C_1-C_{10} linear or branched alkylene, C_3-C_{20} arylene, C_4-C_{20} alkyl substituted arylene, C_4-C_{20} alkylarylene, and mixtures thereof; with a polymer core having *n* functional groups capable of reacting with said non-symmetrical initiator to form a conjugate having the formula:

$$[R—N=N—L—A']_n—[Core]$$

wherein A' is a linking unit to said polymer core;

b) heating said conjugate to a temperature sufficient to form a free radical conjugate having the formula:

$$[\cdot L—A']_n—[Core]$$

said temperature from about 0 °C to about 160 °C;

B) propagating polymerization by adding to said free radical conjugate a least one monomer capable of forming a polymer;

C) polymerizing said monomer in the presence of said free radical conjugate to form a polymer; and

D) terminating polymerization of said monomer.

The present invention further relates to a process comprising the steps of:

A) initiating polymerization with a non-symmetrical initiator comprising the steps of:

a) reacting a non-symmetrical initiator having the formula:

$$R—N=N—L—A$$

wherein R is a unit which is capable of forming a stable free radical and not initiating a free radical polymerization reaction, preferably R is a substituted or unsubstituted triphenylmethyl unit; A is a unit which is capable of reacting with a polymer core functional group thereby providing a means for attaching said non-symmetrical initiator to a polymer core; L is a unit capable of forming a free radical moiety having the formula:

$$\cdot L —$$

said L unit is a substituted or unsubstituted: C_1-C_{10} linear or branched alkylene, C_3-C_{20} arylene, C_4-C_{20} alkyl substituted arylene, C_4-C_{20} alkylarylene, and mixtures thereof; with a polymer core having *n* functional groups capable of reacting with said non-symmetrical initiator to form a conjugate having the formula:

$$[R—N=N—L—A']_n—[Core]$$

wherein A' is a linking unit to said polymer core;

b) heating said conjugate to a temperature sufficient to form a free radical conjugate having the formula:

$$[\cdot L—A']_n—[Core]$$

said temperature from about 0 °C to about 160 °C;

B) adding to said free radical conjugate a least one monomer capable of forming a polymer;

C) adding one or more stable free radical agents;

D) propagating polymerization at the site of said free radical conjugate to form a polymer; and

E) terminating polymerization of said monomer.

The first step of the initiation process involves reacting a non-symmetrical free radical initiator with a polymerization core to form a conjugate. The polymerization cores of the present invention may be mono-functional or polyfunctional as described herein. The conjugate is formed by any reaction or under any conditions which all the free radical initiator to bond with the core without causing the fragmentation of the initiator portion. The formation of the conjugate can be undertaken in the presence of one or more monomers, said monomers ultimately forming the desired polymer, the reaction to form which is being initiated.

The conjugate can be formed *in situ* and the monomer addition which constitutes general process step (b) can then ensue or the conjugate once formed in step (a) can be isolated and purified, especially in the case wherein it is necessary to control the number of initiators per equivalent of core material or in the case wherein sequential polymerization is to be

accomplished. For the purposes of the present invention the term "sequential polymerization" is defined herein as polymers which are built up by a series of polymerization reactions using different monomers, mixtures of monomers, or ratios of monomer for each sequence. A non-limiting example of a polymer formed sequentially comprises a core having the formula:

$$HO—[CORE]—O[protecting\ group]$$

which is reacted with a non-symmetrical initiator having the formula:

$$R—N{=}N—L—CO_2H$$

to form a conjugate, said conjugate is further reacted with *n* equivalents of monomer HZ to form a polymer or oligomer having the formula:

$$H(Z)_n—L—\overset{\overset{O}{\|}}{C}—O—[CORE]—O[protecting\ group]$$

which is subsequently de-protected and reacted with another equivalent of the non-symmetrical initiator and *m* equivalents of a monomer HY to form the sequential polymer having the formula:

$$H(Z)_n—L—\overset{\overset{O}{\|}}{C}—O—[CORE]—O—\overset{\overset{O}{\|}}{C}—L—(Y)_mH$$

wherein from the same core two different polymer chains derived from two different monomers have been formed.

Step (b) or the initiation process or polymerization process of the present invention can be conducted in the presence of a solvent or without a solvent. A solvent may be used in step (a) to facilitate the formation of the conjugate and may optionally be left in the reaction mixture to aid in the solublizing of the reagents which are combined in step (b). A solvent may be used as a carrier to deliver one or more monomers to the reaction vessel in which the polymerization reaction is to take place. A solvent may be used in step (b) and then removed prior to the initiation step which forms the free radical initiator, especially in the case wherein the polymerization is conducted at a temperature above the boiling point of the solvent. Non-limiting examples of solvents include aliphatic alcohols, glycols, ethers, glycol ethers, pyrrolidines, N-alkyl pyrrolidones, polyethylene glycols, polypropylene glycols, amides, carboxylic acids, esters, organosulfides, sulfoxides, sulfones, alcohol derivatives, hydroxyether derivatives, amino alcohols, ketones, aromatics, and the like. Specific non-limiting examples include ethylene glycol, propylene glycol, diethylene glycol, glycerin, dipropylene glycol, tetrahydrofuran, and the like. Particularly preferred solvents include N,N-dimethylformamide (DMF), benzene, toluene, *tert*-butylbenzene, dioxane, and primary alcohols such as methanol, ethanol, *n*-propanol, *iso*-propanol, and *n*-butanol. Among these, N,N-dimethylformamide, benzene, toluene, dioxane, *n*-

butanol, and *tert*-butylbenzene are more preferred, particularly N,N-dimethylformamide, benzene, *n*-butanol, and *tert*-butylbenzene. Solvents, may be use to adjust the viscosity of the reaction mixture.

The free radical forming step of the initiation process or of the polymerization process is conducted at a temperature which breaks down the non-symmetrical initiator liberating a molecule of nitrogen gas, a stable free radical R and a free radical L moiety which is capable of initiating polymerization, said fragmentation having the general scheme:

$$R{-}N{=}N{-}L{-}A'{-}O{-}[CORE] \longrightarrow \cdot L{-}A'{-}O{-}[CORE] + N_2 + R\cdot$$

wherein this fragmentation can occur in the presence of a monomer or absent a monomer.

The polymer propagation step of the polymerization process of the present invention may be conducted at any temperature which enables free radical polymerization, preferably from about 0 °C to about 160 °C. At lower temperatures (typically from about 0 °C to about 30 °C), radiation such as ultraviolet radiation may be required for displacement of the tritylazo moiety. Preferably, the polymer is formed through heating at a temperature from about 60 °C, more preferably from about 70 °C, most preferably from about 90 °C to about 160 °C, more preferably to about 120 °C, most preferably to about 115 °C. The polymer is most preferably formed below the decomposition temperature of the stable free radical agent. For example, DEPN is known to decompose above 120 °C. The temperature at which the reaction is conducted may be modified throughout formation of the polymer, *i.e.*, the temperature may be decreased or increased as the ordinary artisan determines necessary. For example, as additional or different monomer is added (*e.g.*, wherein a block copolymer is being formed), cooling may be required prior to introducing such monomer. As another example, the temperature may need modification depending upon the success of the reaction, *i.e.*, whether the reaction is progressing too rapidly or not rapidly enough.

A preferred polymerization process of the present invention utilizes stable free radical agents (SFRA's) to modulate the process, said process comprising the steps of:

A) initiating polymerization with a non-symmetrical initiator comprising the steps of:
   a) reacting a non-symmetrical initiator according to the present invention with a polymer core to form a conjugate;
   b) heating said conjugate to a temperature sufficient to form a free radical conjugate;

B) propagating polymerization by adding to said free radical conjugate a least one monomer capable of forming a polymer and at least one stable free radical agent (SFRA);

C) polymerizing said monomer in the presence of said free radical conjugate and said stable free radical agent to form a polymer; and

D) terminating polymerization of said monomer.

Example of stable free radical agents are well known in the art and are used to modulate the polymerization by controlling the kinetic and/or thermodynamic conditions under which polymerization occurs. Non-limiting examples of stable free radical agents are described in U.S. 5,498,679 Moffat et al., issued March 12, 1996; U.S. 5,412, 047 Georges et al., issued May 2, 1995;

EP 0 773 232 published May 14, 1997; EP 0 869 137 published October 7, 1991; EP 0 735 064, published October 2, 1996; EP 0,844,256 published May 27, 1998; EP 0 807 640 published November 19, 1997; WO 97/46593; WO 96/024620; WO 98/13392 published April 2, 1998; "Controlled Free-Radical Polymerization In the Presence of a Novel Asymmetric Nitroxyl Radical", Benoit et al., *Polymer Preprints*, Vol. 38, No. 1, pp. 729 - 730 (1997); "The Reaction of Acyl Peroxides with 2,2,6,6-Tetramethylpiperidinyl-1-oxy", Moad et al., *Tetrahedron Letters*, Vol. 22, pp. 1165 - 1168 (1981); "Synthesis and Applications to 'Living' Free Radical Polymerization of a New Class of Nitroxyl Radicals", Grimaldi et al., *Polymer Preprints*, Vol. 38, No. 1, pp. 651 - 652 (1997); "Improved Methods for the Oxidation of Secondary Amines to Nitroxides", Rauckmann et al., *Synthetic Communications*, pp. 409 - 413 (1975); "Total Control", Schrope, *New Scientist*, February 20, 1999, pp. 40 - 43; all of which are incorporated herein by reference.

Non-limiting examples of preferred stable free radical agents for use in the present invention are nitroxides. As the ordinarily skilled artisan will be aware, such nitroxides are either commercially available or synthesized according to known methods. For example, the synthesis of nitroxides from amine precursors is described by Rozantsev and Sholle, in *Synthesis*, pp. 190 - 202 (1971) and "Improved Methods for the Oxidation of Secondary Amines to Nitroxides", Rauckmann et al., *Synthetic Communications*, pp. 409 - 413 (1975). Other compounds which are useful as stable free radical agents according to the processes of the present invention include the dithioesters disclosed in WO 98/01478 published January 15, 1998 and WO 99/05099 published February 4, 1999 both of which are included herein by reference.

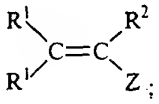
The following are preferred stable free radical agents: 2,2,5,5-tetramethylpyrrolidine nitroxide (PROXYL); 2,2,6,6-tetramethyl-1-piperidine nitroxide (TEMPO); diisobutyl nitroxide (DTBN); N-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (DEPN).

In the embodiment of the present invention wherein a stable free radical agent is utilized, said agent is present in an amount which will modulate the reactivity of the propagating site. Preferably, the molar ratio of stable free radical agent to initiating site will range from about 1 : 1 (SFRA : initiating site) to about 3 : 1 (SFRA : initiating site), more preferably from about 1.1 : 1 to about 2 : 1, even more preferably from about 1.1 : 1 to about 1.7 : 1, and most preferably from about 1.1 : 1 to about 1.5 : 1. Any stable free radical agent known in the art may be utilized according to the present invention. Preferred stable free radical agents are set forth herein below.

Monomers

The monomers or mixtures of monomers which are suitable for use in the processes of the present invention are any which are capable of polymerizing via a free radical mechanism.

Examples of preferred monomers of the present invention have the formula:



wherein each R^1 is independently

a) hydrogen;

b) C_1-C_4 alkyl;

c) substituted or unsubstituted phenyl;

d) substituted or unsubstituted benzyl;

e) carbocyclic;

f) heterocyclic;

g) and mixtures thereof;

each R^2 is independently

a) hydrogen;

b) halogen

c) C_1-C_4 alkyl;

d) C_1-C_4 alkoxy;

e) substituted or unsubstituted phenyl;

f) substituted or unsubstituted benzyl;

g) carbocyclic;

h) heterocyclic;

i) and mixtures thereof;

each Z is independently

a) hydrogen;

b) hydroxyl;

c) halogen;

d) $-(CH_2)_mR$;

wherein R is:

i) hydrogen;

ii) hydroxyl

iii) halogen;

iv) nitrilo;

v) $-OR^3$;

vi) $-O(CH_2)_nN(R^3)_2$;

vii) $-O(CH_2)_nN^+(R^3)_3X^-$;

viii) $-OCO(CH_2)_nN(R^3)_2$;

ix) $-OCO(CH_2)_nN^+(R^3)_3X^-$;

x) $-NHCO(CH_2)_nN(R^3)_2$;

xi) $-NHCO(CH_2)_nN^+(R^3)_3X^-$;

xii) $-(CH_2)_nN(R^3)_2$;

xiii) $-(CH_2)_nN^+(R^3)_3X^-$;

xiv) carbocyclic;

xv) heterocyclic;

xvi) nitrogen heterocycle quaternary ammonium;

xvii) nitrogen heterocycle N-oxide;

xviii) aromatic N-heterocyclic quaternary ammonium;

xix) aromatic N-heterocyclic N-oxide;

xx) -NHCHO;

xxi) or mixtures thereof;

each R^3 is independently hydrogen, C_1-C_8 alkyl, C_2-C_8 hydroxyalkyl, and mixtures thereof; X is a water soluble anion; the index n is from 0 to 6

e) $-(CH_2)_mCOR'$

wherein R' is

i) $-OR^3$;

ii) $-O(CH_2)_nN(R^3)_2$;

iii) $-O(CH_2)_nN^+(R^3)_3X^-$;

iv) $-NR^3(CH_2)_nN(R^3)_2$;

v) $-NR^3(CH_2)_nN^+(R^3)_3X^-$;

vi) $-(CH_2)_nN(R^3)_2$;

vii) $-(CH_2)_nN^+(R^3)_3X^-$;

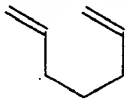
viii) or mixtures thereof;

each R^3 is independently hydrogen, C_1-C_8 alkyl, C_2-C_8 hydroxyalkyl, and mixtures thereof; X is a water soluble anion; the index n is from 0 to 6;

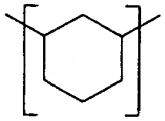
f) and mixtures thereof;

the index m is from 0 to 6;

The monomers of the present invention may also comprise cyclically polymerizing monomers, a non-limiting example of which is the diene having the formula:



which results in a polymer or co-polymer having units with the formula:



Preferred vinyl aromatic monomers include styrene, α-methylstyrene, 3,4-dimethylstyrene, 4-methylstyrene, 2-chlorostyrene, 3-methylstyrene, 3-chlorostyrene, 4-methoxystyrene, 4-chloro-3-methylstyrene, 2-hydroxymethylstyrene, 3-(*tert*-butyl)styrene, 4-chloro-3-methylstyrene, 2,4-dichlorostyrene, 4-ethylstyrene, 2,6-dichlorostyrene, 4-ethoxystyrene, 1-vinylnapthalene, vinyltoluene, 2-vinylpyridine, 4-vinylpyridine, 2-vinylnapthalene, 1-α-methylvinylnapthalene, 2-α-methylvinylnapthalene, 1,2-diphenyl-4-methylhexene-1, 3,5-diethylstyrene, 2-ethyl-4-benzylstyrene, 4-phenylstyrene, 4-*p*-tolylstyrene, 2,4-divinyltoluene, 4,5-dimethyl-1-vinylnapthalene, divinyl benzene, styrene sulfonic acid, vinylbenzoic acid, and 4-(*tert*-butyl)styrene.

Preferred acryl monomers include ethyl acrylate, cyclohexyl acrylate, propyl acrylate, *iso*-decyl acrylate, *iso*-propyl acrylate, phenyl acrylate, butyl acrylate, norbornyl acrylate, *iso*-butyl acrylate, *iso*-bornyl acrylate, hexyl acrylate, alkylthioalkyl acrylates, *tert*-butyl acrylate, alkoxyalkyl acrylates, 2-ethylhexyl acrylate, methoxyethyl acrylate, nonyl acrylate, ethoxyethyl acrylate, lauryl acrylate, acrylonitrile, stearyl acrylate, dialkylacrylamide, methyl acrylate, pentyl acrylate, hexyl acrylate, 3,3-dimethoxypropyl acrylate, 3-methacryloxypropyl acrylate, 2,2,3,3,4,4,4-heptafluorobutyl acrylate, ethyl 2-cyanoacrylate, 4-fluorophenyl acrylate, 2-methacryloxyethyl acrylate, propyl vinyl ketone ethyl 2-chloroacrylate, 2-(1-propenyl)oxylethyl acrylate, allyl acrylate, acrylic acid, β-methylacrylic acid (crotonic acid), α-phenylacrylic acid, N,N-dimethyl acrylamide, glyceryl acrylate, α-cyanoacrylic acid, hydroxyethyl acrylate, sorbyl acrylate, 2-(dimethylamino)ethyl acrylate, hydroxymethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, acrylamide, methylol acrylamide, gamma trimethoxy silyl propyl acrylate, isocyanato ethyl acrylate, *tert*-butyl amino ethyl acrylate, diethylamino ethyl acrylate, 2-

phenoxyethyl acrylate, phenylbutyl acrylate, benzyl acrylate, acrylonitrile, glycidyl acrylate, octyl acrylate, 2-carboxyethyl acrylate, 2-sulfoethyl acrylate, N-methoxy methylol acrylamide, and N-butoxy methylol acrylamide.

Preferred methacryl monomers include methyl methacrylate, 2-ethylhexyl methacrylate, ethyl methacrylate, cyclohexyl methacrylate, 2,2,2-trifluoroethyl methacrylate, octyl methacrylate, *n*-propyl methacrylate, *iso*-octyl methacrylate, *iso*-propyl methacrylate, decyl methacrylate, *n*-butyl methacrylate, hydroxyethyl methacrylate, *sec*-butyl methacrylate, hydroxypropyl methacrylate, *tert*-butyl methacrylate, norbornyl methacrylate, *n*-amyl methacrylate, *iso*-bornyl methacrylate, *iso*-amyl methacrylate, methacrylonitrile, hexyl methacrylate, diallylmethacrylamides, pentyl methacrylate, nonyl methacrylate, lauryl methacrylate, 2-acetoxyethyl methacrylate, *p*-tolyl methacrylate, glycidyl methacrylate, 3-methoxypropyl methacrylate, 2(1-propenyl)oxylethyl methacrylate, 2-(trimethyloloxy)ethyl methacrylate, allyl methacrylate, methacrylic acid, glyceryl methacrylate, hydroxyethyl methacrylate, 2-(dimethylamino)ethyl methacrylate, sorbyl methacrylate, hydroxybutyl methacrylate, hydroxymethyl methacrylate, hydroxypropyl methacrylate, methacrylamide, isocyanato ethyl methacrylate, methylol methacrylamide, gamma trimethoxy silyl propyl methacrylate, *tert*-butyl amino ethyl methacrylate, diethylamino ethyl methacrylate, phenyl methacrylate, methacrylonitrile, glycidyl methacrylate, dodecyl methacrylate, 2-carboxyethyl methacrylate, 2-sulfoethyl methacrylate, and 2-phosphonoethyl methacrylate.

Preferred conjugated diene monomers include 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 2-methyl-6-methylene-2,7-octadiene (myrcene), 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-pentadiene, 1,3-hexadiene, 2-methyl-1,3-hexadiene, 1,3-heptadiene, 3-methyl-1,3-heptadiene, 1,3-octadiene, 3-butyl-1,3-octadiene, 3,4-dimethyl-1,3-hexadiene, 3-*n*-propyl-1,3-pentadiene, 4,5-diethyl-1,3-octadiene, 2,4-diethyl-1,3-butadiene, 2,3-di-*n*-propyl-1,3-butadiene, 2-methyl-3-*iso*-propyl-1,3-butadiene, piperylene, methylpentadiene, phenylbutadiene, isoprene (2-methyl-1,3-butadiene), 2-ethyl-1,3-butadiene, 2-propyl-1,3-butadiene, 2-butyl-1,3-butadiene, 2-pentyl-1,3-butadiene, 2-hexyl-1,3-butadiene, 2-heptyl-1,3-butadiene, 2-octyl-1,3-butadiene, 2-nonyl-1,3-butadiene, 2-decyl-1,3-butadiene, 2-dodecyl-1,3-butadiene, 2-tetradecyl-1,3-butadiene, 2-hexadecyl-1,3-butadiene, 2-isoamyl-1,3-butadiene, 2-phenyl-1,3-butadiene, 2-methyl-1,3-pentadiene, 2-methyl-1,3-hexadiene, 2-methyl-1,3-heptadiene, 2-methyl-1,3-octadiene, 2-methyl-1,3-nonyldiene, 2-methyl-1,3-decyldiene, and 2-methyl-1,3-dodecyldiene.

Other preferred monomers for use in the present invention include tetrafluoroethylene, hexafluoropropylene, perfluoro(alkyl vinyl ethers), 2-methacryloxyethyl linoleate, diallyl maleate, diallyl fumarate, diallyl phthalate, 2-(3-isopropenylphenyl)-2-isocyanatopropane, vinyl

acetate, vinyl propionate, vinyl butanoate, 3-butenoic acid, 2-acrylamido-2-methyl-propane sulfonic acid (AMPS), methallyl sulfonic acid, vinyl sulfonic acid, 2-acrylamido-2-methyl-propane phosphonic acid (AMPS), vinyl phosphonic acid, vinyl pyridine, methylene malononitrile, propylene, chloroprene, vinyl chloride, vinyl bromide, vinyl fluoride, vinylidene chloride, methyl vinyl ether, vinyl napthalene, 2-vinyl pyrrole, 3-vinyl pyrrole, 2-vinyl oxazole, 4-vinyl oxazole, 2-vinyl thiazole, 4-vinyl thiazole, 2-vinyl imidazole, 4-vinyl imidazole, 3-vinyl pyrazole, 4-vinyl pyrazole, 3-vinyl pyridazine, 4-vinyl pyridazine, 3-vinyl isoxazole, 4-vinyl isoxazole, 3-vinyl isothiazole, 4-vinyl isothiazole, 2-vinyl pyrimidine, 4-vinyl pyrimidine, 5-vinyl pyrimidine, 2-vinyl pyrazine, isobutene, vinyl N-alkylpyrroles, N-vinyl pyrrolidones, maleic acid, itaconic acid, maleic anhydride, β-acryloxy propionic acid, cinnamic acid, *p*-chloro cinnamic acid, 1-carboxy-4-phenyl-1,3-butadiene, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, fumaric acid, tricarboxy ethylene, methylene malononitrile, itaconic anhydride, and methacryol isocyanate.

Still other preferred monomers useful in the present invention include silicon group containing monomers, including pentamethyldisiloxanylpropyl methacrylate, heptamethyltrisiloxanylethyl acrylate, phenyltetramethyldisiloxanylethyl acrylate, *iso*-butylhexamethyltrisiloxanylpropyl methacrylate, methyldi(trimethylsiloxy)-methacryloxymethylsilane, *n*-propyloctamethyltetrasiloxanyl propyl methacrylate, *tert*-butyltetramethyldisiloxanylethylacrylate, *n*-pentylhexamethyltrisiloxanylmethyl methaerylate, vinyltrimethoxysilane, vinyltriethoxysilane, vinyl-tris (2-methoxy-ethoxy) silane, 3-acryloxyethyltrimethoxysilane, 3-acryloxypropyltrimethoxysilane, 3-acryloxypropylmethylmethoxysilane, 3-methacryloxypropylmethyldiethoxysilane, and 3-methacryloxypropyltriethoxysilane.

The following are non-limiting examples of the process of the present invention.

The polymer thus prepared according to the present method can, if desired, be isolated from the reaction mixture by standard methods well-known to the ordinarily skilled artisan. For example, the polymer may be isolated by precipitation utilizing a solvent in which the polymer is not soluble.

The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity of the polymers prepared according to the present invention are analyzed by conventional processes.

EXAMPLE 2

A flask is charged with Starburst® (PAMAM) Dendrimer, Generation 1 (commercially available from Aldrich Chemical Co. as a 20% solution in methanol, and having 8 surface primary amine groups). The methanol is concentrated to give 1.43 g of the dendrimer. The

dendrimer is dissolved in N,N-dimethylformamide (DMF, 140 mL) and diisopropylethylamine (4.14 mL), the (tritylazo)functionalized compound of Example 1 (3.45 g), and O-(7-azabenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU, commercially available from Perseptive Biosystems, Hamburg, Germany or Aldrich Chemical Co., Milwaukee, WI) is sequentially added.

This mixture is stirred under a drying tube for 17 hours at 25 °C. The DMF is substantially removed by rotary evaporation *in vacuo*. The resulting oil is re-dissolved in dichloromethane (15 mL) and slowly added to a well-stirred mixture of ether:dichloromethane (4:1, 625 mL). The liquids are decanted from the product which is then re-dissolved in dichloromethane (25 mL). Another ether:dichloromethane mixture (3:1, 1100 mL) is added. The mixture is stirred for 30 minutes. The resulting precipitate is collected by filtration. Re-precipitation is performed as above to provide the functional initiator which is utilized without further purification.

EXAMPLE 3

A flask is charged with an oligomeric 1:1 copolymer of methyl methacrylate and hydroxymethyl methacrylate, weight average molecular weight, 14,400 (360 mg). Dichloromethane is added (15 mL), followed by dimethylaminopyridine (30.5 mg), the (tritylazo)functionalized compound of Example 1 (740 mg in 15 mL dichloromethane), and dicyclohexylcarbodiimide (387 mg). The mixture stirs for about 18 hours at 25 °C.

The reaction mixture is filtered to remove the resulting urea by-product, and then concentrated *in vacuo* to approximately a 10 mL volume. The solution is slowly added to a well-stirred portion of ether (500 mL). The ether is decanted and the product is washed with more ether and isolated to give the desired functional initiator having approximate esterification of 88% of the hydroxyl groups.

EXAMPLE 4

A flask is charged with Starburst® (PAMAM) Dendrimer, Generation 2 (commercially available from Aldrich Chemical Co. as a 20% solution in methanol, and having 16 surface primary amine groups). The methanol is evaporated under reduced pressure to yield approximately 490 mg of dendrimer. The dendrimer is dissolved in N,N-dimethylformamide (10 mL) followed by an excess of N,N-diisopropylethylamine and an excess of the (tritylazo)functionalized compound of Example 3b (bromide). With a drying tube attached, the mixture is stirred for approximately 48 hours. The N,N-dimethylformamide is removed under high vacuum. The resulting oil is taken up in methanol and re-precipitated to provide a functional

initiator having 32 arms due to double addition of the bromide to each of the surface primary amine groups.

EXAMPLE 5

A 250 mL flask is charged with the linear oligomer aminopropylmethylsiloxane - dimethylsiloxane copolymer having MW = 40,800 (24 g, commercially available from Gelest Inc.), dichloromethane (150 mL), dimethylaminopyridine (101 mg, 0.82 mmol), and the compound of Example 1 (2.42 g, 6.2 mmol). To that solution, with stirring at 25 °C, is added dicyclohexylcarbodiimide (1.27 g, 6.18 mmol) in one portion. After stirring for 17 hours at 25 °C, the solution is filtered (removing the urea byproduct) and concentrated *in vacuo* to give a yellow oil. The oil is dissolved in dichloromethane (100 mL) and added dropwise to methanol (1 L) while swirling. The methanol is then decanted and the oily product is washed with more methanol (4 x 1 L). The resulting oil is purified by filtration through a column of basic alumina using dichloromethane as eluent. The product is then concentrated *in vacuo* to give the functional initiator as a viscous, yellow oil. The functional initiator gives a negative ninhydrin test.

EXAMPLE 6

To a reactor is charged N-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxyl (DEPN; 0.29 g, 1 mmol) the functional initiator of Example 2 (0.1 mmol), butyl acrylate (40 g, 313 mmol), and approximately 2.5 mL of N,N-dimethylformamide. This mixture is repeatedly degassed with vacuum and re-pressurized with nitrogen gas and immersed in an oil bath at 110 °C for 16 hours. The resulting polymer is diluted with tetrahydrofuran and then isolated by precipitation into a water:methanol (10:90, v:v) mixture and vacuum dried. The polymer is characterized by GPC analysis utilizing refractive index, light scattering and differential viscosity detectors.

EXAMPLE 7

To a reactor is added DEPN (0.044 g, 0.15 mmol), the functional initiator of Example 3 (0.012 mmol), and styrene (5 g, 48 mmol). This mixture is repeatedly degassed with vacuum and re-pressurized with nitrogen gas and immersed in an oil bath at 120 °C for 22 hours. The polymer is isolated by precipitation into methanol and vacuum dried. The polymer is characterized by GPC analysis utilizing refractive index, light scattering and differential viscosity detectors.

EXAMPLE 8

To a reactor is added 0.05 g (0.15 mmol) of di(thiobenzoyl)disulfide (prepared as described in Rizzardo et al., WO 99/05099, assigned to E.I. Du Pont De Nemours, published February 4, 1999), 0.012 mmol of the functional initiator of Example 2, and 5 grams (0.048 mol) of styrene. This mixture is degassed with vacuum, re-pressurized with nitrogen gas, and immersed in an oil bath at 100 °C for 22 hours. The resulting star polymer is diluted with tetrahydrofuran and then isolated by precipitation into methanol and vacuum dried. The polymer is characterized by GPC analysis utilizing refractive index, light scattering, and differential viscosity detectors.

EXAMPLE 9

To a reactor is added 0.05 g (0.15 mmol) of di(thiobenzoyl) disulfide, 0.012 mmol) of the functional initiator of Example 2, and 5 grams (0.04 mol) of butyl acrylate. This mixture is degassed with vacuum, re-pressurized with nitrogen gas, and immersed in an oil bath at 100 °C for 22 hours. The resulting polymer is diluted with tetrahydrofuran and then isolated by precipitation into a methanol/water (9/1 v/v) mixture and vacuum dried. The polymer is characterized by GPC analysis utilizing refractive index, light scattering, and differential viscosity detectors.

EXAMPLE 10

To a reactor is added 0.05 g (0.15 mmol) of di(thiobenzoyl) disulfide, 0.012 mmol) of the functional initiator of Example 3, and 5 grams (0.05 mol) of methyl methacrylate. This mixture is degassed with vacuum, re-pressurized with nitrogen gas, and immersed in an oil bath at 60 °C for 22 hours. The resulting polymer is diluted with tetrahydrofuran and then isolated by precipitation into methanol and vacuum dried. The polymer is characterized by GPC analysis utilizing refractive index, light scattering, and differential viscosity detectors.

What is claimed is:

1. A process for initiating polymerization comprising the steps of:

a) reacting a non-symmetrical initiator having the formula:

$$R—N=N—L—A$$

wherein R is a unit which forms a free radical which does not initiate polymerization; A is a unit which is capable of reacting with a polymer core functional group thereby providing a means for attaching said non-symmetrical initiator to a polymer core; L is a unit capable of forming a free radical moiety having the formula:

$$\cdot L—$$

said L unit is a substituted or unsubstituted: C_1-C_{10} linear or branched alkylene, C_3-C_{20} arylene, C_4-C_{20} alkyl substituted arylene, C_4-C_{20} alkylarylene, and mixtures thereof; with a polymer core having *n* functional groups capable of reacting with said non-symmetrical initiator to form a conjugate having the formula:

$$[R—N=N—L—A']_n—[Core]$$

wherein A' is a linking unit to said polymer core;

b) adding to said conjugate a least one monomer capable of forming a polymer to form a reaction mixture; and

c) initiating polymerization by heating said reaction mixture to a temperature sufficient to form a free radical conjugate having the formula:

$$[\cdot L—A']_n—[Core]$$

said temperature from 0 °C to 160 °C.

2. A process for polymerization comprising the steps of:

A) initiating polymerization with a non-symmetrical initiator comprising the steps of:

a) reacting a non-symmetrical initiator having the formula:

$$R—N=N—L—A$$

wherein R is a unit which forms a free radical which does not initiate polymerization; A is a unit which is capable of reacting with a polymer

core functional group thereby providing a means for attaching said non-symmetrical initiator to a polymer core; L is a unit capable of forming a free radical moiety having the formula:

$$\cdot L —$$

said L unit is a substituted or unsubstituted: C_1-C_{10} linear or branched alkylene, C_3-C_{20} arylene, C_4-C_{20} alkyl substituted arylene, C_4-C_{20} alkylarylene, and mixtures thereof; with a polymer core having *n* functional groups capable of reacting with said non-symmetrical initiator to form a conjugate having the formula:

$$[R—N=N—L—A']_n—[Core]$$

wherein A' is a linking unit to said polymer core;

b) heating said conjugate to a temperature sufficient to form a free radical conjugate having the formula:

$$[\cdot L—A']_n—[Core]$$

said temperature from 0 °C to 160 °C;

B) propagating polymerization by adding to said free radical conjugate a least one monomer capable of forming a polymer;

C) polymerizing said monomer in the presence of said free radical conjugate to form a polymer; and

D) terminating polymerization of said monomer.

3. A process for polymerization comprising the steps of:

A) initiating polymerization with a non-symmetrical initiator comprising the steps of:

a) reacting a non-symmetrical initiator having the formula:

$$R—N=N—L—A$$

wherein R is a unit which forms a free radical which does not initiate polymerization; A is a unit which is capable of reacting with a polymer core functional group thereby providing a means for attaching said non-symmetrical initiator to a polymer core; L is a unit capable of forming a free radical moiety having the formula:

$\cdot L-$

said L unit is a substituted or unsubstituted: C_1-C_{10} linear or branched alkylene, C_3-C_{20} arylene, C_4-C_{20} alkyl substituted arylene, C_4-C_{20} alkylarylene, and mixtures thereof; with a polymer core having *n* functional groups capable of reacting with said non-symmetrical initiator to form a conjugate having the formula:

$$[R-N=N-L-A']_n-[Core]$$

wherein A' is a linking unit to said polymer core;

b) heating said conjugate to a temperature sufficient to form a free radical conjugate having the formula:

$$[\cdot L-A']_n-[Core]$$

said temperature from 0 °C to 160 °C;

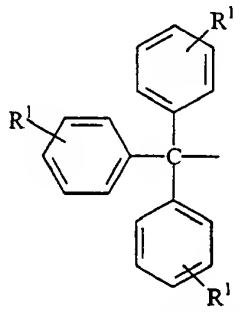
B) adding to said free radical conjugate a least one monomer capable of forming a polymer;

C) adding one or more stable free radical agents;

D) propagating polymerization at the site of said free radical conjugate to form a polymer; and

E) terminating polymerization of said monomer.

4. A process according to any of Claims 1-3 wherein R has the formula:



wherein each R^1 is independently selected from the group consisting of:

a) hydrogen;

b) C_1-C_{12} alkyl;

c) C_3-C_{12} cycloalkyl;

d) C_3-C_{15} substituted or unsubstituted aryl;

e) C_4-C_{15} substituted or unsubstituted alkylenearyl;
f) $-N(R^2)_2$;
g) $-OR^2$;
h) $-SR^2$;
i) and mixtures thereof;
wherein each R^2 is independently selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, C_3-C_{15} substituted or unsubstituted aryl, C_4-C_{15} substituted or unsubstituted alkylenearyl, and mixtures thereof.

5. A process according to any of Claims 1-4 wherein said L unit is a nitrile substituted unit.

6. A process according to any of Claims 1-5 wherein said A unit is selected from the group consisting of $-CO_2H$, $-NH_2$, -OH, halogen, and mixtures thereof.

7. A process according to any of Claims 1-6 wherein said core is selected from the group consisting of polyfunctional aromatic compounds, saccharides, polyols, calixaranes, dendrimers, polyamines, ammonia, and mixtures thereof.

8. A process according to any of Claims 1-7 wherein said process is conducted in the presence of a solvent selected from the group consisting of aliphatic alcohols, glycols, ethers, glycol ethers, pyrrolidines, N-alkyl pyrrolidones, polyethylene glycols, polypropylene glycols, amides, carboxylic acids, esters, organosulfides, sulfoxides, sulfones, alcohol derivatives, hydroxyether derivatives, amino alcohols, ketones, aromatics, and mixtures thereof.

9. A process according to any of Claims 1-8 further comprising one or more stable free radical agents.

10. A non-symmetrical free radical polymerization initiator having the formula:

$$R-N=N-L-A$$

wherein R is a unit which forms a free radical which does not initiate polymerization; A is a unit which is capable of reacting with a polymer core functional group thereby providing a means for attaching said non-symmetrical initiator to a polymer core; L is a unit capable of forming a free radical moiety having the formula:

-L—

said L unit is a substituted or unsubstituted: C_1-C_{10} linear or branched alkylene, C_3-C_{20} arylene, C_4-C_{20} alkyl substituted arylene, C_4-C_{20} alkylarylene, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

Int. ..tional Application No
PCT/US 00/12700

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F4/04 C08F2/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category '	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NORIO TSUBOKAWA ET AL: "GRAFT POLYMERIZATION OF METHYL METHACRYLATE INITIATED BY PENDANT AZO GROUPS INTRODUCED ONTO Y-POLY(GLUTAMIC ACID)" , JOURNAL OF POLYMER SCIENCE, POLYMER CHEMISTRY EDITION,US,JOHN WILEY AND SONS. NEW YORK, VOL. 31, NR. 2, PAGE(S) 563-568 XP000335491 ISSN: 0887-624X the whole document ---	1-3,5-10
X	US 4 048 423 A (MACLEAY RONALD EDWARD ET AL) 13 September 1977 (1977-09-13) the whole document ---	1-3,5-10
X	US 3 987 024 A (MACLEAY RONALD EDWARD ET AL) 19 October 1976 (1976-10-19) the whole document ---	1-3,5-10
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 August 2000	08/08/2000

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INTERNATIONAL SEARCH REPORT

Int. .tional Application No
PCT/US 00/12700

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 021 480 A (RAVICHANDRAN RAMANATHAN) 4 June 1991 (1991-06-04) the whole document -----	10

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Int. .tional Application No
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